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**RECOVERY OF METALS BY ION FLOTATION
FROM DILUTE AQUEOUS SOLUTIONS**

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ABSTRACT

Flotation, a process originating from the minerals industry, is finding its way as a separation process for dilute aqueous solutions, with particular interest in metal ions recovery. The present paper reviews the several flotation techniques available in this area, with certain illustrative laboratory examples. Metals investigated are the following: chromium, copper, zinc, arsenic, lead, iron and germanium. The various parameters affecting the process are examined and attention is paid towards the selectivity of the process.

CONTENTS

1. INTRODUCTION
2. BUBBLE GENERATION METHODS
 - 2.1 Dispersed-Air flotation
 - 2.2 Dissolved-Air Flotation
 - 2.3 Electrolytic Flotation
3. FLOTATION TECHNIQUES
 - 3.1 Foam Flotation
 - 3.2 Ion Flotation
 - 3.3 Precipitate flotation
 - 3.4 Adsorbing colloid flotation
4. MAIN PROCESS PARAMETERS
 - 4.1 Reagents concentration
 - 4.2 Gas Flowrate
 - 4.3 Temperature
 - 4.4 pH of Solution
 - 4.5 Ionic Strength
 - 4.6 Metal Ion Concentration
5. OPERATION AND DESIGN ASPECTS
6. SELECTIVE SEPARATION BY FLOTATION
7. REFERENCES

ACKNOWLEDGEMENTS

NOMENCLATURE

1. INTRODUCTION

Flotation is a separation process that originated in the field of mineral processing, more than a century ago; it has been established since as one of the most significant methods for the concentration and dressing of ores and industrial minerals. It is estimated that approximately two million tons of ore are beneficiated each year by flotation ¹.

Herodotus, in ancient Greece, is probably the first person that described a process similar to flotation, in the 5th century B.C., for the separation of gold particles from sand using fatty substances ². Later, in the 15th century A.D., the Arabs used

resins for the selective separation of azurite from gangue. These are considered to be the historical roots of flotation.

The basic principles of the process are very simple. Most of the minerals are naturally hydrophilic (talc and sulfur are among the few exceptions). If in a mixture of particles, therefore, some of them are or are artificially made to be hydrophobic, they tend to separate; the presence of bubbles of air fed into the apparatus helps in that these particles attach themselves to the surface of the bubbles and are thus floated to the top of the vessel. Usually, the overflowing stream contains the useful component of the mixture, whereas the underflow (termed the "tailings") carries the undesirable particles ("gangue"). The case when the desirable component flows in the tailings is termed "reverse flotation".

Compared to other mineral processing methods (e.g. tables, jigs, heavy media, magnetic separation, etc.), particle size has to be quite small (less than 500 μm), in order to be floated. The small size and the intense agitation of the "pulp" (solid-liquid dispersion) helps particles coming into contact with bubbles so that they may float. The small size is also helpful in liberating the useful mineral, especially for complex mineralogy.

Flotation is beneficial not only to minerals and pyrite separation from coal, but to a large variety of chemical species too, e.g. ions, molecules, microorganisms etc. : they can either be separated from one another or concentrated from solution. The technique used in these cases is collectively termed "adsorptive bubble separation techniques" (see the work of Grieves, Rubin and their teams ³) and is based upon the differences in surface activity of the various substances, that are present in a solution or suspension.

As opposed to (minerals) froth flotation, this technique requires aeration at a lower gas flowrate. Another major difference is the species concentration which is much lower (sometimes a few ppm), in comparison with a solids content of 20% to 40% of mineral particles in the former. Extensive bibliography in the area exists (e.g. Somasundaran ⁴ and Clarke and Wilson ⁵).

In the seventies, the idea of using rising gas bubbles in a separation process was applied successfully in effluent treatment. The various metal production and finishing operations, power plants, chemical industries etc. use large quantities of contact process water and the spent streams generally contain moderate concentrations of heavy metal ions, which have to be removed. This process, however, has proved useful lately as a method for selectively recovering metal ions from dilute solutions, e.g. from the leaching of lean minerals.

The aim of the present paper is to describe the recent advances and innovations of the flotation process. The applications reviewed will serve as examples merely to explain the different techniques, based on our experience, and do not intend to cover the entire literature.

2. BUBBLE GENERATION METHODS

In some industrial processes, for instance in plating industries, a large proportion of the plating metals are discharged in the form of effluent rather than being collected and recycled. The value of the metal lost is quite high, but the failure to reuse the water may represent (in the near future) a much greater loss⁶. A range of processes is available to separate and possibly recover metals from dilute solutions. The selection of the right process depends certainly on economics, but particular situations have to be taken into consideration also, such as composition, throughput and even the local discharge limits. Usually, a metal-bearing sludge or similar product is produced, which contains metals in a concentrated form. The latter is rarely suitable for metals recovery and its disposal may present a pollution hazard⁷.

Flotation constitutes an alternative process, which offers the advantages of concentration and separation in one operation. Its main requirement is the generation of small gas bubbles and the use of an appropriate surfactant. The size of the bubbles is of major importance in flotation⁸, with preference in very small

bubbles, often less than 100 μm . It should be noted that this agrees with the maximum bubble size for complete laminar flow, which was calculated ⁹ and found to be 130 μm .

A photographic technique has been used ¹⁰ to measure the size of the bubbles in flotation. A special camera was constructed, based on earlier trials in solvent extraction, with a suitable lens having a long probe (0.33m in length), whose end was immersed in the flotation cell at a certain angle, to photograph the dispersion with proper illumination. The size of the bubbles was then measured by projecting the film, with a total magnification of approximately 200 times.

According to the method used for the generation of bubbles, two broad categories of flotation process exist: the dispersed-air and the dissolved-air flotation.

2.1. Dispersed-Air Flotation

This method generates bubbles by introducing air directly into the flotation cell. In larger agitated cells, air is usually introduced through the bottom of the agitator shaft and small bubbles are obtained mainly by the shearing effect of impellers.

In smaller cells, however, as well in flotation columns, a "sparger" is often used. The material used for the sparger may be rigid (e.g. porous ceramic, stainless-steel or polyethylene) or soft (filter cloth, rubber etc.), whereas its shape may vary (plate or cylinder). The size of the bubbles depends upon the sparger pore size; the performance of rigid porous spargers have tended, however, to deteriorate, due to pore plugging.

A novel design, producing extremely fine bubbles, has been developed by the US Bureau of Mines, discussed in the following section.

Dispersed-air is used mainly in froth flotation, e.g. of sulfide minerals ¹¹. Another example is the processing of magnesite and dolomite (magnesium carbonates) with sodium oleate ¹², salt-type minerals which are relatively little studied.

Typical bench-scale tests for the investigation of the floatability of the pure minerals are carried out in a micro-cell, the Hallimond tube ⁴, having a dispersion volume of approximately 200 cm³. Further experiments are however conducted in larger agitated flotation cells (from 500 to about 4,000 cm³ of pulp), of standard design like e.g. Agitair, Denver, Outokumpu, Wemco, Nagahm, Mekhanobr, Leeds, etc. ^{13,14}.

Recently, a new type of flotation cell, the flotation column, is finding its way ¹⁵, due to certain advantages it offers in extremely small particles ("fines") flotation.

In another application of dispersed-air flotation, a porous dome made of carborundum was used on a flanged base-plate of the flotation vessel ¹⁶; this was connected to a compressor (excess air pressure under the plate 80 mm Hg, air flow 260 cm³.s⁻¹). This system was used to examine the removal of the organic entrainment (LIX reagents) in copper solvent extraction by flotation. The process was foreseen as an intermediate stage between stripping and electrowinning of copper and has since found industrial application ¹⁷.

2.2 Dissolved-Air Flotation

Dissolved-air (or pressure) flotation is based on the varying solubility of air in water, according to the pressure in the vessel. Initially, water is saturated with air at a relatively high pressure. When this water is introduced in the flotation vessel, the change to normal (atmospheric) pressure releases the air bubbles. Alternatively, vacuum may be used to decrease the pressure, after first saturating the water at atmospheric pressure. The amount of air dissolved in water for a given pressure may be easily calculated using Henry's law.

The US Bureau of Mines presented recently a new way of dissolving air into water. This represents an advantage over the

previous batch pressure vessel in that it may be operated continuously ¹⁸.

The technique found an early application in fine coal cleaning in U.K., but was later abandoned ¹⁹. Today, dissolved-air flotation is the established method of bubble generation in effluent treatment, particularly in refineries and, in general, for oil-contaminated surface waters and waste waters ¹⁹.

Design and experimental studies were reported on a pilot plant processing 2,300 m³ per day, which was installed by a Water Company ²⁰ and also in the thickening of activated sludge by dissolved-air flotation. Before entering into the dissolved-air flotation unit, the effluent flows through a flocculation tank, into which coagulating chemicals (such as ferrous or ferric sulfate, lime, alum or polyelectrolytes) are dosed in proportion to the flow rate and concentration. The choice of dosing chemicals generally relies on local conditions and prices.

Dissolved-air flotation has also been applied to magnesium carbonate fines ²¹ (sub-sieve size range). Fines represent a considerable loss of mineral and metal values and new processes are being developed (as well as improving old ones) for the recovery of fine particles. The application of conventional flotation techniques for the separation of mineral fines is generally uneconomical and presents several scientific and technological problems ¹⁹.

The air volume produced from the saturation tank is often of interest and a method for measuring it has been devised ²²: the apparatus consists of two inter-connected glass vessels. Water saturated with air at a relatively high pressure (usually 400-500 kPa) is allowed to flow through a pressure reducing device and then into the first vessel, while at the same time water is displaced from the second one. The volume of water displaced from the second vessel is equal to the volume of water-plus-air added to the first, i.e. the difference of the two measured water volumes gives the released air volume.

2.3 Electrolytic Flotation

Electrolysis of the aqueous part of the pulp generates the gas bubbles (mainly hydrogen and oxygen) in the dispersion, in this case. The technique was developed particularly in the USSR. It has found many applications in industrial effluent treatment²³. It was tried effectively, for example, for the treatment of a liquid waste from a power station, consisting of a mixture of oil, pulverized fly ash and an aqueous solution¹⁰; it was also applied to an emulsion paint dilution and an emulsified oil-water dispersion.

Electrodes of various configurations and materials were tested, including a bipolar set. It was also examined whether the chemical difference of the gases had any effect on the process, by constructing the cell so that the two horizontal electrodes were separated by a cation exchange membrane. If a viable electrolytic flotation process is to be developed, however, electrode materials of adequate mechanical and electrical properties with an extended lifetime should be found²⁴.

The removal of chromium (initial concentration 10 ppm) from dilute solutions was also achieved by electrolytic flotation²⁵, using dodecylamine or cetyltrimethyl-ammonium bromide as collector, at a current density of 200 A m⁻² and 18 V. Chromium has attracted a rather wide attention from researchers in the field of flotation, due to its many uses. Chromium is usually found in liquid wastes from etching and machining operations, metal plating and electroplating, tanning, etc. while chromates are widely used as a corrosion inhibitor in cooling towers. Thus, chromium is considered as a toxic water pollutant (mainly in its hexavalent form). Its removal was also achieved by :

- continuous dissolved-air ion flotation using ethylhexadecyl-dimethylammonium bromide as a collector and a non-ionic polymer²⁶;
- precipitate flotation of chromium by sodium lauryl (dodecyl) sulfate, after reduction of Cr⁺⁶ to Cr⁺³ with ferrous sulfate²⁷; and

- ion flotation of hexavalent chromium by using a cationic collector (rosim amine acetate) ²⁸.

Electrolytic flotation offers certain advantages over the other methods of bubbles generation, i.e. the conventional dispersed-air and the dissolved-air flotation. The electrode grids can be arranged so as to provide good coverage of the whole surface area of the flotation cell avoiding any by-pass. Gas production, flotation time and other operating conditions can be checked quickly and are easily controlled. The equipment is reliable and safe in operation.

3. FLOTATION TECHNIQUES

The classification of the various flotation techniques is already known ⁴ and the basic theoretical principles have also been described elsewhere ^{4,5} ; it is not the aim of the present work to repeat them. In the following, only the main flotation techniques will be discussed. It is stressed, however, that there is some overlapping between them, not only in the terms that have been used by the various workers, but in the actual process itself.

3.1 Foam Flotation

Foam flotation (or foam separation) generally requires the generation of a foam (or froth) to carry off material. This belongs to a sub-category of foam fractionation, which is the foaming off of dissolved material from a solution via adsorption on bubble surfaces - e.g. of a surfactant ³. In contrast, there is another division, with much less applications, the non-foaming techniques as bubble fractionation and solvent sublation ³.

One of the useful characteristics of foam flotation is its ability to concentrate from extremely dilute solutions up to fractions of ppm, possibly too dilute to handle economically by

other means. This is the reason why the process is also used as an analytical technique in the preconcentration step (see, for example, the work of Zeitlin ⁵).

Foam flotation has also been applied to particulate-solution systems, such as bacteria, ferric oxide, clays etc. ³. Recently, the technique was applied to zeolites ²⁹; they are often used, among other applications, for the ion exchange of metal ions (e.g. Zn ions ²⁹). Their separation and recovery from solid/liquid dispersions may present several difficulties if conventional processes like sedimentation or filtration are used, mainly because of their fine particle size (85% of synthetic NaY were found in the range $-5.5+1.9 \mu\text{m}$). It was proved experimentally that the foam flotation of zeolites by cationic collectors at pH values around 7.6 was possible giving a satisfactory removal. A mean residence time of the order of 10 min for dispersed-air flotation was found to be really fast in comparison to sedimentation.

3.2 Ion Flotation

The technique was actually introduced by the late Felix Sebba ³⁰. Later, Pinfold published an excellent review ³. Ion flotation involves the removal of surface-inactive ions from aqueous solutions by adding surfactants (termed also collectors) and the subsequent passage of air bubbles through the solutions. As a result of this flotation procedure, a solid particle containing the surfactant as a chemical constituent appears on the surface of the solution. This permits the separation and concentration of the ionic species in a small volume of collapsed foam.

If the foam is stable and needs to be broken, various chemical, thermal or mechanical methods may be used. The surfactant is usually an ion having a charge opposite to that of the surface-inactive ion (sometimes termed colligend); thus, cations and anions are floated with anionic and cationic surfactants, respectively. The surfactants are generally recoverable from the ion-

surfactant product (sublate), so in principle they may be easily recycled in the process. Otherwise, this may preclude the use of this technique for large scale operations, mainly without economic benefit, as in effluent treatment.

When the sublate reaches ultimately the surface of the solution, it is always present as a solid. Prior to this, however, it may comprise groups of ions held to the surface of the bubble by the surface activity of the surfactant. The ion concentrations are usually low and flotation occurs from a true ionic solution.

Raising the concentrations may lead to precipitation of the product to be removed, before gas is passed into the solution; this means that it is not a solution anymore, but rather a dispersion of extremely fine solid particles. Ion flotation carried out under these conditions is a form of the technique known as precipitate flotation (see section 3.3 below).

Many pollutants in industrial wastewaters are charged colloids. Their removal requires, as a pretreatment step, coagulation or adsorption, the next step usually being filtration (or sedimentation) of the formed colloid, which is especially slow. The same technique may be applied to certain types of uncharged pollutants, with the addition of hydrolyzable salts, prior to the pretreatment step.

Ion flotation has been proposed as an alternative to this slow - process. The charged colloids may be floated with surfactants carrying the opposite charge, due to electrostatic interaction. This technique is called adsorbing colloid flotation and has been developed mainly by Wilson and co-workers⁵.

Hence, both precipitate flotation and adsorbing colloid flotation can be considered, in the broad sense, as an evolution of ion flotation.

A simple system for illustrating ion flotation is perhaps the removal of the hexavalent chromium ion from dilute aqueous solutions. Dodecylamine was used as the cationic surfactant, in an ethanolic solution³¹; both dissolved- and dispersed-air methods were tried for concentrations up to 90 ppm. The addition of sur-

factant in the form of an ethanolic solution is a usual practice³, since it allows the simultaneous addition of ethanol, which acts as a frother, although it is not a typical one. This practice is followed because the surfactants usually used are not very soluble and it is convenient to maintain them in solution until they may come into contact with the ions.

The amount of surfactant needed in ion flotation is directly related to the amount of the metal to be removed (surface-inactive ion) and its state, and generally is not influenced by the amount of solution. At least, a stoichiometric amount is required theoretically.

The aquatic chemistry and speciation of the metal may be important and should be examined, too^{3,2}. Hexavalent chromium is extensively hydrolyzed in water, giving only neutral or anionic species. All the equilibria occur rapidly depending on the concentration, with $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- or H_2CrO_7 (in higher concentrations) dominating in acidic and CrO_4^{2-} in basic solutions.

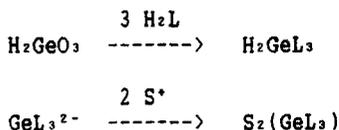
It is possible, however, that the surface-inactive ion (for instance, a slightly dissociated acid) may require first an activator as a ligand in order to form a strong acid; then, the whole complex could float by adding a surfactant. This is another form of ion flotation and shall be illustrated for the Ge case.

Germanium is known to be a scattered element occurring in traces in other ores, mainly mixed sulfides and coal. In many countries, fly ash (the pulverised fuel ash from coal fired power plants) is used as raw material for germanium, since the combustion process concentrates germanium. It has been reported, too, that germanium occurs in mixed sulfides in the processing plant of Tsumeb, in S. Africa².

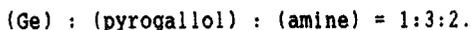
Among the main recovery methods of germanium from concentrates is a hydrometallurgical route (possibly in combination with pyrometallurgy), which usually results in the production of aqueous solutions in which germanium coexists with other metal ions (as arsenic, lead, zinc, etc.).

Concentration and separation of germanium from aqueous solutions are of technological importance, but the available methods suffer from a number of disadvantages. For instance, precipitation of germanium by tannin substances presents the unfavorable effect of tannin on zinc electrolysis³³. Various separation methods were published³⁴ on the recovery of germanium in aqueous solutions, such as distillation, solvent extraction, ion exchange, precipitation, etc. The recovery of germanium in a bench-scale cell (120 cm³) by ion flotation has been proposed again as an alternative method^{32,33}, as well as being a characteristic example of the technique.

Pyrogallol, a poly-hydroxy-compound known to form a strong complex acid with germanium in dilute solutions of the following composition (H₂Ge)L₃ - where L is the ligand - was tested as an activator. It was assumed that this complex acid, which dissociates forming (GeL₃)²⁻ anions, may be floated with cationic surfactants, such as amine-type substances (in this case, dodecylamine). So, if S⁺ denotes the cation of the surfactant, ion flotation of germanium was shown to follow a mechanism of the form :



which was certified by an elemental analysis (of N, C and H)³³. This means that the stoichiometric ratio is :



A 10% excess of reagents over this theoretical ratio was used. Figure 1 present some of the results using dispersed-air^{32,34}. It should be noted that removal or recovery by flotation (R ; [%]) is usually expressed as

$$R = \{1 - (C/C_0)\} \times 100$$

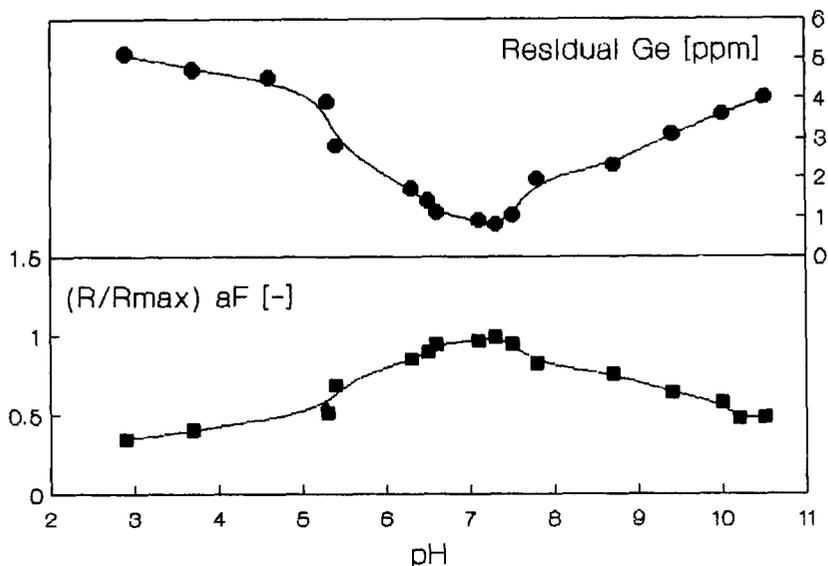


FIGURE 1

Influence of pH on flotation activity of germanium and on its concentration in the solution remaining after flotation ³⁴. Reagents used : pyrogallol (ligand) and dodecylamine (surfactant). Reprinted with permission; copyright 1987 Elsevier Science Publishers.

where C_0 denotes the initial concentration and C the concentration at time t .

Other work on Ge flotation involves the flotation of tannate and gallate complexes, of citrato- and tartrato-germanic acid, and also of trihydroxo-fluoronate complexes with a cationic surfactant ³⁵.

Another example of ion flotation is the removal of copper or zinc ³⁶ in acidic medium. Among the various collectors, O-alkyl dithiocarbonates (usually termed xanthates) are known to exhibit a high level of chemical reactivity for heavy metals, either in solution or at sulfide mineral surfaces ¹³. Dialkyl-dithiocarbamates, which exhibit similar properties - i.e. precipitation of

metals as highly insoluble complexes - have been used widely in analytical chemistry, but applications as collectors are rather limited, obviously due to costs ³⁷.

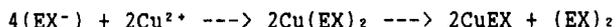
Monolauryl dithiocarbamate has been found to be a weak chelating agent for the removal of copper ³⁸. In contrast, xanthate systems have often been studied for flotation practice, as the copper ion removal by the so-called IPU (ion-precipitate-ultrafine) process ³⁹; soluble copper xanthate complexes have also been examined ⁴⁰.

Thio collectors offer the further advantage that the collector and frother actions can be controlled independently. They do not adsorb actively at the air/liquid interface, mainly because of their short hydrocarbon chains and the high aqueous solubilities of their anionic forms. Lack of significant chain association also explains the inability of dissolved thio anions to form colloidal minerals that could be detrimental to flotation.

The particle size of the precipitate obtained with addition of the xanthate in cupric salt solutions depends on the concentration of reagents. Since the size of a precipitate is an effective parameter in flotation, the pretreatment conditions in a mixing tank have been examined ³⁶, in order to produce the appropriate floc size for flotation.

The rate of preliminary mixing of a solution containing 50 ppm copper ions and an almost stoichiometric amount of potassium ethyl xanthate (denoted as KEX) was examined. At 400 rpm initial mixing for 10 min, acceptable flotation removals of the order of 90% was obtained. The use of a 10% excess of xanthate improved the results. The pH of solution did not affect the process from a value of 2.5 to about 5.5. A xanthate analysis of the remaining solution was also conducted ³⁶; the introduction of a surfactant in an effluent containing a metal to be removed should not obviously add a new pollutant! However, no xanthate was detected. The remaining copper in solution under optimum operating conditions was under 1 ppm - usually, an acceptable level.

The reaction of dissolved copper with xanthate anions (homogeneously, heterogeneously, or electrocatalytically) gives an unstable complex, which decomposes to produce dixanthogen and cuprous xanthate; both precipitate out of solution as an agglomerate :



Diethyl-dithiocarbamate has also been tried successfully as a collector for copper and zinc ions separately ³⁶. Copper ion removal by dissolved-air flotation was found to be feasible in the pH range of approximately 2 to 6, whereas the zinc ion was effectively removed above pH approximately 4.

The type of process applied above for copper and zinc removal could also be termed precipitate flotation of the "third kind", according to Pinfold ³; i.e. the precipitate formed contains the collector as a chemical constituent and floats like in ion flotation.

3.3 Precipitate Flotation

Following the forementioned classification which, however, was not universally accepted, the two other categories are as follows :

- (i) Precipitate flotation of the "first kind" involves the flotation of precipitate particles by a surface-active species; the latter is not a chemical constituent of the precipitate substance and occurs only on the surface of the particles.
- (ii) Precipitate flotation of the "second kind" uses no surfactant to float the particles but two hydrophilic ions precipitate to form a solid with a hydrophobic surface.

Generally, precipitate flotation is a process that involves concentration of the ionic species by forming initially some kind of precipitate and removal of the precipitate from the dilute

aqueous dispersion by transfer to surface by gas bubbles. In this way, heavy metals can be removed or separated by flotation, usually in the form of their hydroxides, as for instance in the case of chromium ⁴¹. The advantage of precipitate flotation over the strictly speaking ion flotation is the lower surfactant requirement.

The precipitation of heavy metals as sulfides is known to present some advantages as compared to hydroxides (usually produced by lime addition). Earlier research in the field referred to the precipitation and removal of heavy metals as sulfides ⁴², the foam and bubble fractionation of dissolved copper ⁴³, the adsorbing colloid flotation of both copper and zinc from seawater ⁴⁴ and the precipitate flotation of copper sulfide ⁴⁵.

The technique has been applied to the CuS/ZnS system ⁴⁶; this was later extended to continuous flow operation in the laboratory ⁴⁷, in a cell with a content of about 2,100 cm³, also to be discussed later. Dodecylamine was used both as a coagulant and as a collector, while the addition of small amounts of cetylpyridinium chloride was necessary in the latter, in order to obtain a stabler froth. Trivalent chromium was also precipitated as a hydroxide and (foam) floated in continuous flow ⁴⁸.

In industrial wastewater treatment, the conventional method for heavy metals removal is to precipitate the ion as a hydroxide which is then removed by settling of the precipitate. Several metal ion solutions may be processed by precipitate flotation as hydroxides. For instance, lead has been removed from dilute solutions (initial concentration 10⁻⁴ M) at a pH of approximately 9 using dodecylamine as a collector ⁴⁹. It was found that the curve of flotation removal versus the pH of solution was similar to the theoretical curve showing the region of Pb(OH)₂ precipitation, based on hydrolysis data. Lead hydroxide has also been removed by foam separation using sodium dodecylsulfate ⁴⁹, while germanium has been separated from lead ⁵⁰.

Zinc ions were removed from dilute aqueous solutions satisfactorily by dispersed-air precipitate flotation as hydroxide ⁵¹.

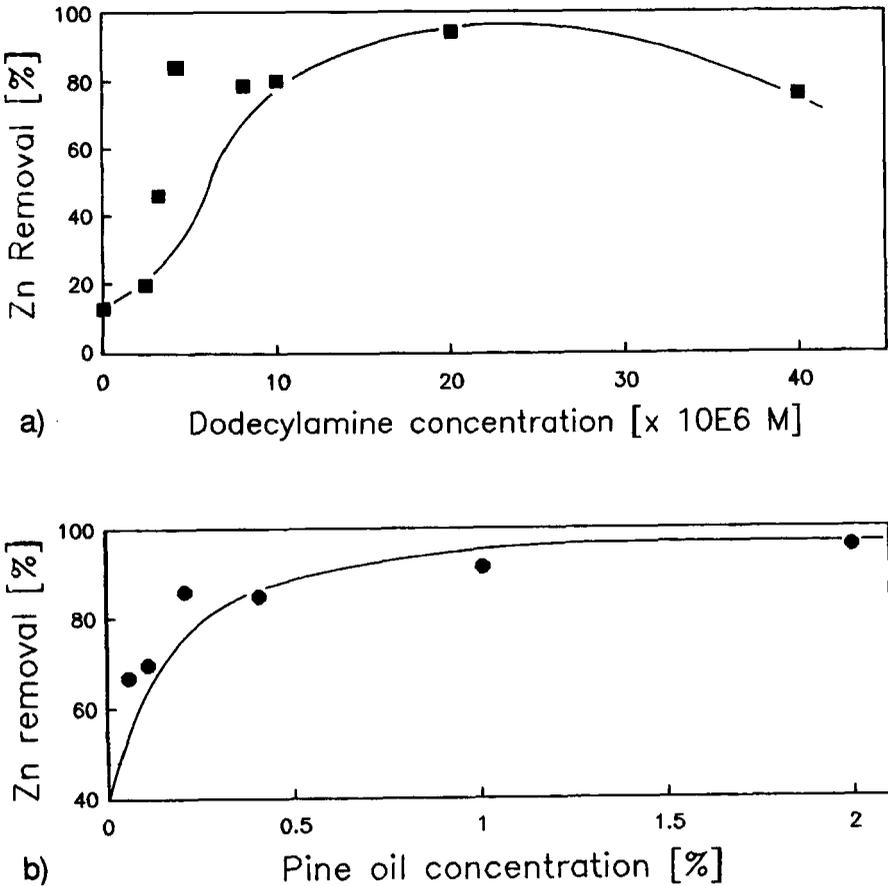


FIGURE 2

Precipitate flotation of Zn. Effect of concentration of the added reagent (a) dodecylamine, (b) pine oil⁵¹. Reprinted with permission; copyright 1987, Technical Chamber of Greece.

Dodecylamine and fatty acids were used as collectors (cationic and anionic, respectively), after pH was properly adjusted.

In Fig. 2 some of the results are illustrated. It is interesting to note the effect of the addition of a widely-used former, pine oil : zinc removals of over 90% were achieved by the addition

of pine oil alone (at a concentration of the order of 1%), i.e. without any collector. This indicates that zinc hydroxide precipitate is highly hydrophobic.

Zinc ions have also been removed by :

- foam fractionation as a cyanide complex anion ⁵²,
- ion flotation as a chloride anion ⁵³ or in thiocyanate solutions ⁵⁴ (both with cationic surfactants).

Various bubble generation methods have been applied : dissolved-air ⁵⁵ or electrolytic generation ⁵⁶.

The application of the above work could be extended to the mining/metallurgical industry. For instance, during the processing of mixed sulfide ores, dissolved zinc exists in froth flotation waters, its concentration depending on the pH value. This happens because zinc sulfate is usually added at the grinding stage, together with other sphalerite (ZnS) depressing reagents ⁵⁷. A change of pH (due to the pyrite introduction) may cause the precipitation of zinc hydroxide, which then cover the sulphides or gangue particles surface.

Heavy metals may be removed by precipitation not only as hydroxides, but as sulfides, too. Solubility favours sulfide precipitation, since the lower solubility of metal sulfides improves the efficiency of metal removal. Also, in hydroxide precipitation, the minimum solubilities for various metals occur at different pH values and the hydroxide precipitates are amphoteric in nature. Often, the presence of complexing agents, such as ammonia or EDTA, prevents the effective precipitation ⁴². Other advantages of the sulfide precipitation are that the sludge produced exhibits better thickening properties and dewaterability, and is less subject to leaching than metal-hydroxide sludge, therefore final disposal is easier and safer ⁵⁸.

The precipitation of dissolved metals in aqueous solutions as sulfides, being the first stage of the process examined ⁴⁶, may be described as follows :



where M denotes the metal ion. The reactivity of sulfides (S^{2-} , HS^-) with heavy metal ions is high ⁴². The sulfide precipitation techniques are usually restricted to the soluble sulfide method. This involves the addition of Na_2S or NaHS solutions to effluents whereas the insoluble method uses a sparingly soluble metal sulfide as a source of sulfide ions, e.g. freshly prepared FeS . The latter requires large amounts of FeS , adding to the cost of chemicals for the process, and also generates much sludge due to iron. A semi-soluble method by CaS is often encountered.

Many effluents and leaching solutions - possible candidates for the application of the techniques described here - are acidic in nature. The processing for the ion precipitation as sulfides may be done in the original pH of the solution. This means that it is possible to avoid expending large amounts of alkaline reagents for pH adjustment (in the case of hydroxide precipitation) and even added capital costs to the system. To obtain good precipitation results, however, a 130% dosage of sodium sulfide has been found necessary, in relation to the existing copper concentration ⁴⁵.

With the soluble sulfide method, the rate of addition of the sulfide solution may be based either on periodic analyses of the metal content of the solution or it may be continuously varied by monitoring the ion content of the solution using ion-specific electrodes.

A disadvantage of this method is the potential further pollution by H_2S or excess sulfide ions; care should be taken therefore against it. Another disadvantage of this method, too, is that it produces colloidal or very fine particles, which generally settle poorly. The particle size has been determined in the laboratory by using a microfilter; it was found that the precipitated copper

sulfides were retained with a filter having a pore diameter of 0.05 μm .

The extremely small particle size meant that dissolved-air flotation had to be applied; selective flotation of copper and zinc as sulfides from dilute solutions was thus achieved, for concentrations ranging from 50 to 250 ppm, at a value of pH approximately 2⁴⁶. With a stoichiometric amount of collector added to the solution, it was found - by chemical analysis of the solution - that a large proportion of the collector was not removed in the foamate, remaining in solution. So, a small amount of amine (10 ppm) was added to the solution.

The stabilization of the foam was achieved by adding a small amount (1 cm^3) of cetylpyridinium chloride. It was also found that the removal of dodecylamine in the foam layer was independent of the pH of solution.

3.4 Adsorbing Colloid Flotation

For historical reasons, adsorbing colloid flotation is examined last, according to its development. This technique involves the removal of a solute by adsorption on or coprecipitation with a carrier floc, which is then floated after the addition of a suitable surfactant. It should be noted that the processes of adsorption, coprecipitation and occlusion are difficult to distinguish and are often non-selective, thus precluding the possibility for a metal recovery from a mixture. However, it has been stated⁵ that adsorbing colloid flotation, like precipitate flotation, requires less surfactant as it does not react with the solute. Generally, an optimization of the technique to be applied is needed.

An example of adsorbing colloid flotation is the removal of trivalent arsenic³² using dispersed-air. Ferric (and aluminium) sulfate were used as "collectors" to produce the necessary carrier flocs. The ferric hydroxo-complexes, which are produced from the hydrolysis of ferric sulfate, are known³ to be positively charged

at pH values ranging from approximately 2.5 to 9, depending upon the solution conditions. Therefore, sodium oleate was used as an (anionic) collector. Removals of the order of 90% were obtained.

The examination of the arsenic speciation in dilute solutions has revealed the formation of undissociated arsenious acid HAsO_2 at pH values between 1 and 8; at pH values above 8 solubility increases. It was experimentally found that, for pH ranging from 5 to 9, the precipitate produced by the ferric hydroxo-complexes was in a colloidal state, which meant that it would be difficult to remove the solid particles either by filtration or by settling.

The most likely mode of removal, in this case, was thought to be occlusion⁵⁹. Usually, occlusion is restricted to include only phenomena such as ion entrapment, lattice substitution and solid solution formation. Even so, occlusion is vague, hard to measure and not easy to distinguish from adsorption in rapid precipitations.

Many other methods of treatment have been examined, e.g. coagulation, precipitation, bed filtration, lime softening etc.

The adsorbing-colloid technique has also been applied for analytical reasons, i.e. for the concentration of sub-microgram amounts of As. Applications are known both for seawater⁶⁰ and for fresh water⁶¹. It is also expected to remove other heavy metals too (Cu^{2+} , Zn^{2+} etc.), if applied in a mixture⁶⁵.

The technique has been applied for the combined arsenic and germanium flotation removal³⁴, using ferric sulfate / sodium oleate and dispersed-air bubble generation (see Fig. 3). The removal of both arsenic and germanium was observed to decrease at higher initial concentrations of arsenic in the mixture, while the ratio for ferric and oleate was kept at an optimum of 60:15 (ppm) determined experimentally⁶². The most interesting conclusion from this work was that adsorbing colloid flotation was capable of concentrating both elements at the surface, without any selectivity however.

Sodium oleate is an anionic collector, the second most used flotation reagent after dodecylamine. Although it is insoluble

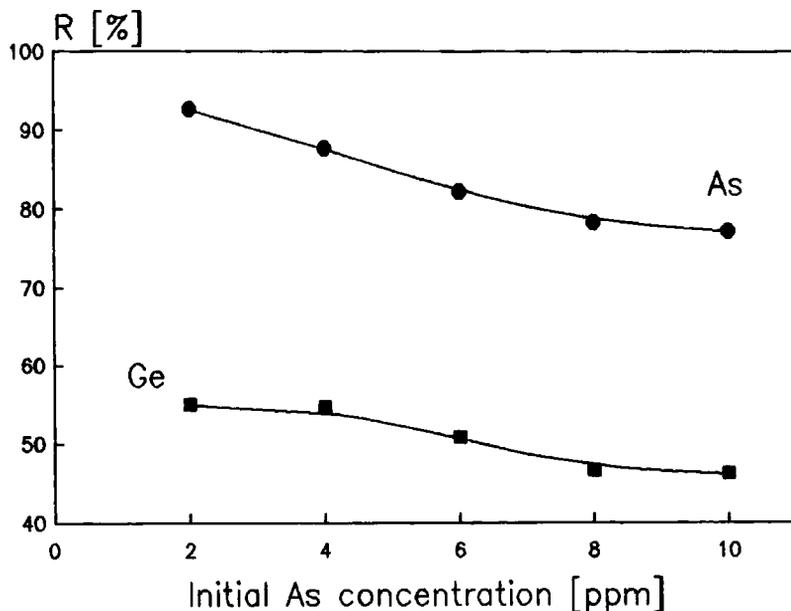
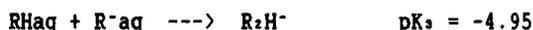


FIGURE 3

Adsorbing colloid flotation of As/Ge mixture. Effect of initial As concentration on recovery ³⁴. Reagents used : ferric hydroxide (carrier floc) and sodium oleate (collector). Reprinted with permission; copyright 1987, Elsevier Science Publishers.

itself, like all fatty acid, it forms very soluble salts with the monovalent ions of alkali-metals. The latter, under suitable conditions, undergo a series of hydrolysis reactions like the following :



where the constants given refer to oleic acid ⁶³. The relative proportion of the various species in an aqueous solution apparently depends on the total concentration of acid, the solution pH, temperature and ionic strength. The behavior of the system is rather complex taking into account the different solubilities of the species in water. Certainly, thermodynamic diagrams would be more helpful for reading.

Adsorbing colloid flotation was also applied in the investigation of the pentavalent arsenic behavior, using hydrolyzed ferric sulfate at a pH value of approximately 5 and initial As concentration ranging from 10 to 100 ppm ³⁶. The solution was agitated at 400 rpm for 10 min, before dispersed-air was introduced into the flotation cell. Removals of the order of 95% were achieved. It should also be noted that the flocs were easily removed, without any need for addition of an anionic surfactant.

Finally, adsorbing colloid flotation has also been applied to lead, using ferric chloride and sodium dodecylsulfate, in a pilot plant ⁶⁴.

4. MAIN PROCESS PARAMETERS

The main parameters affecting the removal of metal ions by flotation will be discussed in the following; a further examination may be found elsewhere ^{3, 65, 66}.

4.1 Reagents Concentration

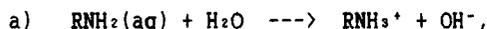
A typical ion flotation process requires a certain amount of collector - at least stoichiometric - in order to remove a given amount of the solution component to be separated. However, in precipitate flotation this is not necessary and much less collector can do the job, as it was shown in Figure 2 for zinc hydroxide where an ethanolic solution of dodecylamine was used. The noti-

ceable removal (approximately 13%), when no collector was added to the system, is probably due to the ethanol presence. Zinc precipitation is achieved after pH is adjusted so that it is in the range from 9 to 9.5 and a combination of reagents is often applied ⁶⁶.

The amount of surfactant and frother (if used) influences the surface tension of solution, too. Surface tension measurements taken while studying the flotation of germanium ³³ showed that while the ethanol concentration increased (added through the dodecylamine solution), the surface tension of the solution decreased, while keeping the collector concentration constant. This had also a significant effect on the process : a decrease in germanium removal was observed, indicating some kind of flotation depression.

The type of collector plays also a significant role. A number of primary aliphatic amines of varying hydrocarbon chain (from 8 to 16 carbon atoms) were tested ³³ for germanium flotation and the highest removal (of the order of 90%) was noticed for dodecylamine.

In the case of primary, secondary or tertiary amines, which are weak bases, the ionization constant is important, as it shows the ratio of ionic species over neutral molecules in the system. For dodecylamine at 298 K the following reactions occur ¹³ :



with

$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2(\text{aq})]} = 4.3 \times 10^{-4}$$



with

$$K_{s0} = [\text{RNH}_3^+][\text{OH}^-] = 8.6 \times 10^{-9}$$



with

$$K_{s1} = [\text{RNH}_2(\text{aq})] = 2 \times 10^{-5}$$

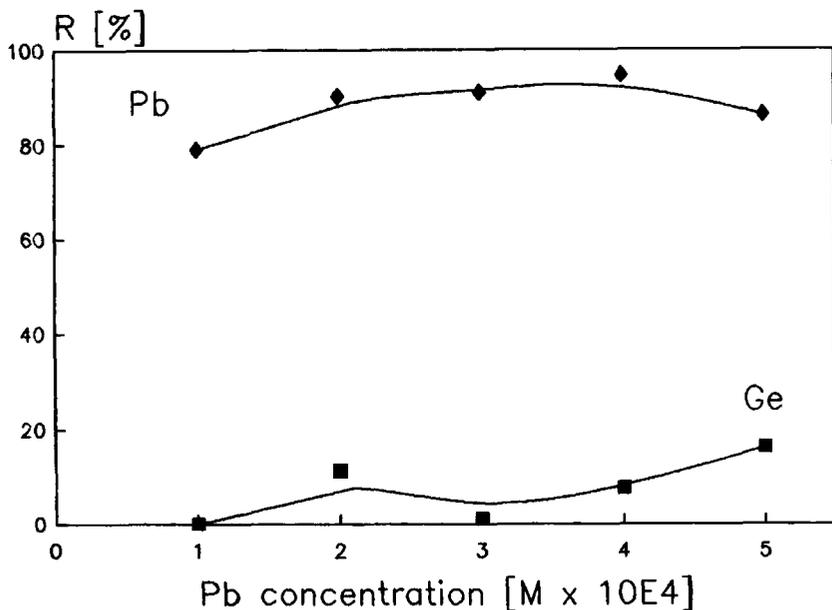


FIGURE 4

Separation of Pb/Ge by dispersed-air flotation. Effect of initial Pb content on flotation ⁵⁰. Collector used : dodecylamine; collector to colligend (lead) ratio : 0.1; Ge concentration 1×10^{-4} M. Reprinted with permission; copyright 1990, Marcel Dekker, Inc.

From these, theoretical curves of concentration versus solution pH may be drawn. It has been found that the pH affects substantially the form of the amine in solution. In acidic solutions, RNH^{3+} dominates and its concentration drops abruptly over the pH of precipitation of $\text{RNH}_2(\text{aq})$. The amount of amine ion RNH^{3+} is usually the collector in the various flotation systems. At a pH of 10.65, for a total amine concentration of 1×10^{-4} M, the species RNH^{3+} and $\text{RNH}_2(\text{aq})$ are present in equal amounts.

During the germanium ion flotation experiments, it was also found that lead ions would cofloat satisfactorily from the dilute solution ⁵⁰ (Fig. 4).

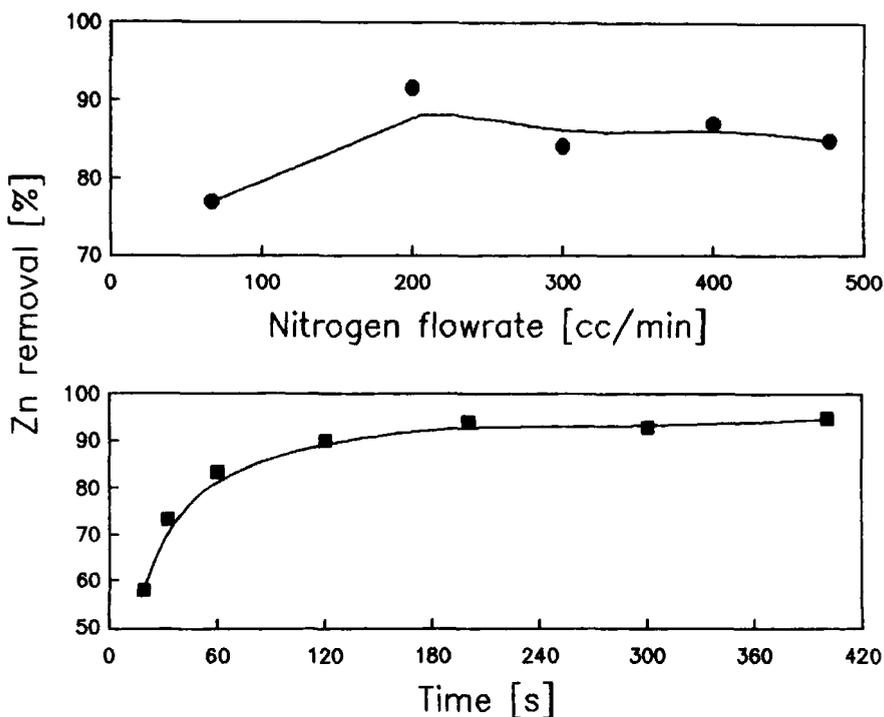


FIGURE 5

Precipitate flotation of Zn as hydroxide using dodecylamine. Effect of gas flowrate and flotation time on removal ⁵¹. Reprinted with permission; copyright 1987, Technical Chamber of Greece.

4.2 Gas Flowrate - Flotation Time

Figure 5 illustrates the effects of nitrogen flowrate (from a nitrogen cylinder) on the flotation of zinc using dodecylamine in a laboratory-scale micro-cell ⁵¹. The cell was made of a glass tube (with an i.d. of 34mm) having at the bottom a gas diffuser made of a Schott D4 glass fritted funnel (with a porosity of 10-16 μm). At gas flowrates above $3.3 \text{ cm}^3 \cdot \text{s}^{-1}$, an almost constant removal rate was observed. The effect of retention time is also shown in Fig. 5; 5 min were found appropriate.

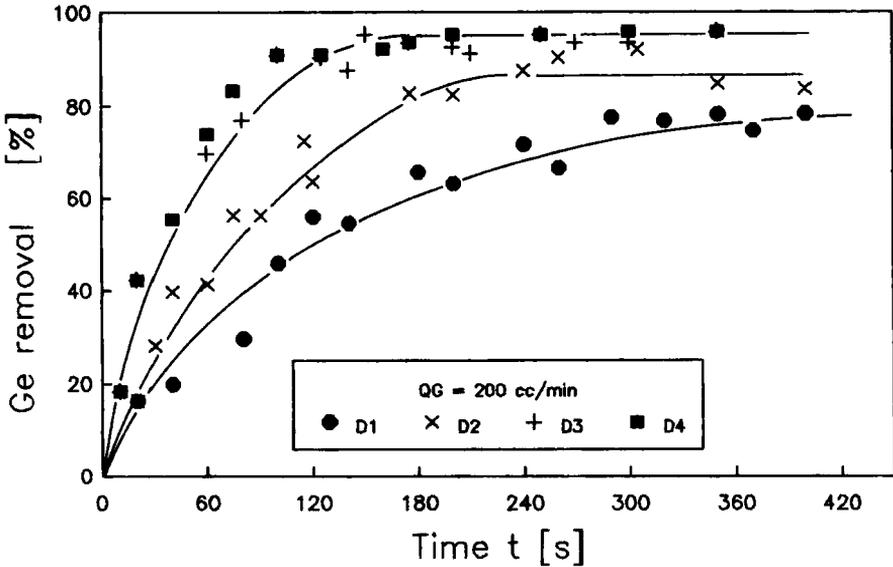


FIGURE 6

Germanium ion removal vs time of flotation for various gas diffuser porosities, with constant gas flowrate ³². Nominal porosity values : D1, 100-160 μm ; D2, 40-100 μm ; D3, 16-40 μm ; D4, 10-16 μm . Reprinted with permission; copyright 1986, Greek Chemists Association.

The bubble size - and hence the flotation efficiency - is influenced not only by the type of diffuser used in the flotation cell, but by the presence of a frother, as well, and to a lesser extent by the presence of a surfactant. Some of them, as sodium oleate, have frothing properties too. For example, in the germanium flotation studies, diffusers with varying porosities were used. An increase in porosity gave better results (Figure 6), since the bubble size decreased resulting in a greater surface area. The largest porosity gave poor flotation results (only 70% removal with the D1); more time was also necessary to reach a steady-state.

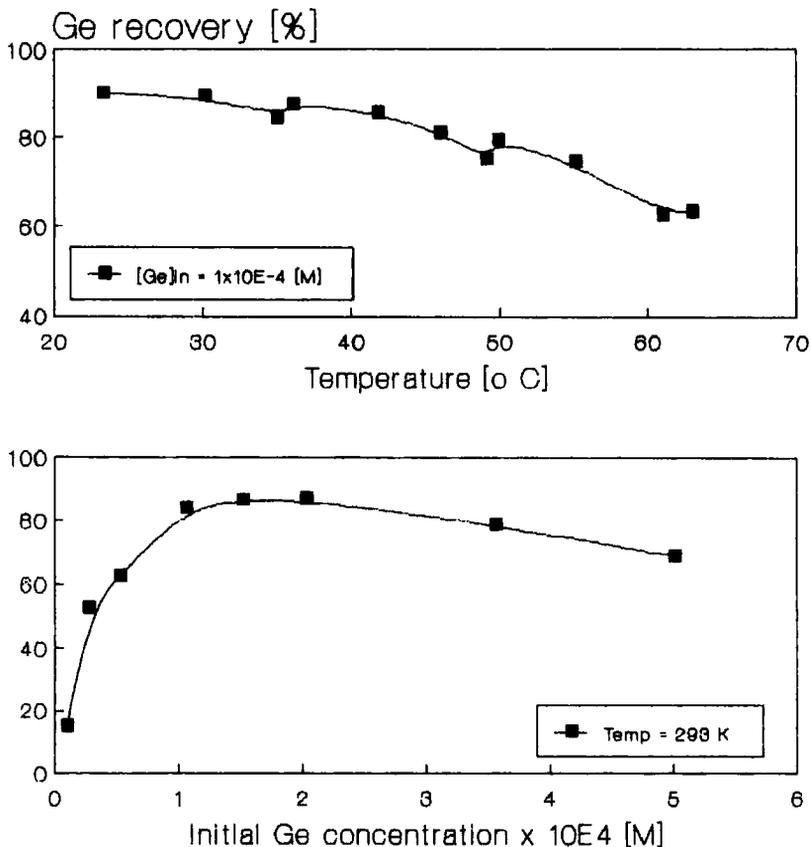


FIGURE 7

Germanium ion flotation : effect of temperature and initial ion concentration on removal ³². [Ge]:[pyrogallol]:[dodecylamine] = 1:3:2. Reprinted with permission; copyright 1986, Greek Chemists Association.

4.3 Temperature

Temperature variations can affect the physico-chemical characteristics of the system like solubility, foam stability, adsorption, etc. However, this is a parameter little examined, possibly due to the appreciable costs involved in providing heat in large scale operations.

Figure 7 shows the effect of temperature on the flotation of germanium. An increase of temperature caused a decrease in germanium removal, probably because adsorption is an exothermic process³. Therefore, an increase in temperature led to a decrease in the amount of collector present on the gas bubble surface. A lower froth stability and higher solubility of precipitate are also expected when temperature increases. On the contrary, in systems where chemisorption prevails, as is the case of fatty acids and their salts, increased recoveries have been noticed².

4.4 pH of Solution

This is the most influential parameter in the flotation process since, depending on the pH value of solution, the flotation process may follow a different route, i.e. through either ion or precipitate flotation. The rate of removal (or recovery) peaks, too, at a certain value of pH, characteristic of each flotation system. This may be found by plotting the removal versus pH; an alternative method is to plot the flotation activity of the ion, a_f . This is calculated as the ratio of the obtained ion removal at any pH over the maximum possible one (for the same system); thus, a_f values lie between 0 and 1.

The effects of pH is illustrated for the case of germanium flotation in Figure 1. It was found that the optimum pH was in the neutral region; outside this area, the recovery rate decreased dramatically. Nearly all the germanium present in solution at low concentrations, at pH from 2 up to 7, exists in the form of metagermanic acid H_2GeO_3 , which is very slightly dissociated and cannot be floated. In alkaline solutions however, anionic forms appear like $Ge(OH)_6^{2-}$. At pH 10, germanium was separated from lead⁵⁰, with Ge remaining in solution. Even in the presence of pyrogallol, germanium had a flotation recovery of less than 40%.

These low recoveries may be attributed to the following: in the alkaline region, oxidation of the ligand (pyrogallol) is expected and the concentration of surfactant cations (dodecylami-

ne) in solution was reduced, due to conversion to neutral molecules, whereas in the acidic region, high foaming was observed and the following effects would be expected:

- (a) the solubility of the precipitate to be high,
- (b) a low degree of ionization of the intermediate complex, and
- (c) an antagonistic action between the introduced anions (from the acidification) and surfactant cations.

Since optimum flotation occurs at a certain pH, which varies from system to system, it is possible to obtain a selective flotation by appropriately controlling pH. For instance, the solution chemistry of dissolved metal ions may be changed by varying the pH, thus precipitating them as hydroxides³⁴.

Additional experiments with corrected pH values, also discussed in the following, were carried out³⁵; it was observed that pH and the ionic strength of solution were related. The addition of salts in order to increase the ionic strength of the solution resulted in a change of pH, due to their hydrolysis.

In the case of lead ion flotation using dodecylamine, the optimum pH region was up to a value of approximately 8⁴⁹; over that pH value, precipitate flotation occurred.

4.5 Ionic Strength

The influence of ionic strength is critical, since it was noticed that it depresses ion flotation^{3,65}. When using a cationic surfactant, an increasing interference was generally observed, in the order :



probably due to an antagonism towards the surfactant cations. However, the following points should be stressed regarding these experiments³³ :

- a) the added salts concentration was enormous, compared to the concentration of the metal ion,

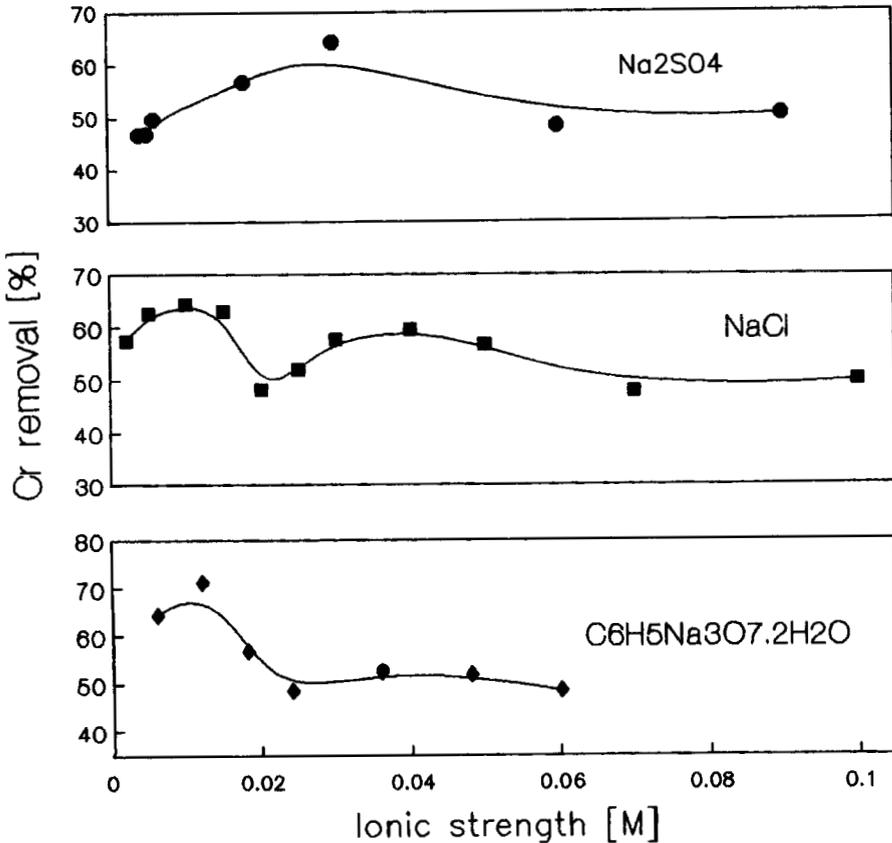


FIGURE 8

Electrolytic flotation of chromium, using dodecylamine. Effect of ionic strength adding sodium salts of chloride, sulfate and citrate²⁵. pH varied, depending upon the addition of salts. Reprinted with permission; copyright 1989, Selper Ltd.

- b) due to this addition, a change in the pH of the solution occurs, moving it far from the optimum value, and
- c) the use of an excess of collector was found to improve flotation results.

The ionic strength of solution was also found to be crucial during the dispersed-air ion flotation of chromium³¹.

Nevertheless, a very interesting observation was made in the case of electrolytic flotation, with the same collector (dodecylamine) as before (Figure 8). It was found that, contrary to what was expected by comparison to other flotation methods, the ionic strength had no significant effect upon the process, even with the noticed high conductivities of 9000 μmhos . The same was also reported for experiments with pH variation ²⁵. This is probably due to the fact that electrolytic flotation is a fundamentally different process, with the electric field gradient between the electrodes. This promotes coagulation and flotation, even without any collector.

4.6 Metal Ion Concentration

The initial cell concentration in batchwise experiments is also important. In Figure 7, an abrupt increase of germanium removal is noticed when its initial concentration reaches an optimum, which is then followed by a decline in ion removal. If plotted in a different way (Figure 9), i.e. showing the concentration of the ion remaining in solution after the dispersed-air flotation, instead of the removal, the actual loss is illustrated.

This parameter in continuous flow systems is termed the feed concentration of the metal to be removed. Figure 10 illustrates some of the results obtained in the precipitate flotation of copper and zinc as sulfides in continuous mode. The dispersed-air method was applied ⁴⁷, leading to a selective separation. Finally, flotation process parameters have been dealt with, in more detail earlier and the potential applications of the process have also been discussed ⁶⁶.

5. OPERATION AND DESIGN ASPECTS

Flotation is a complex process affected by many parameters and the optimum operating conditions are usually established with

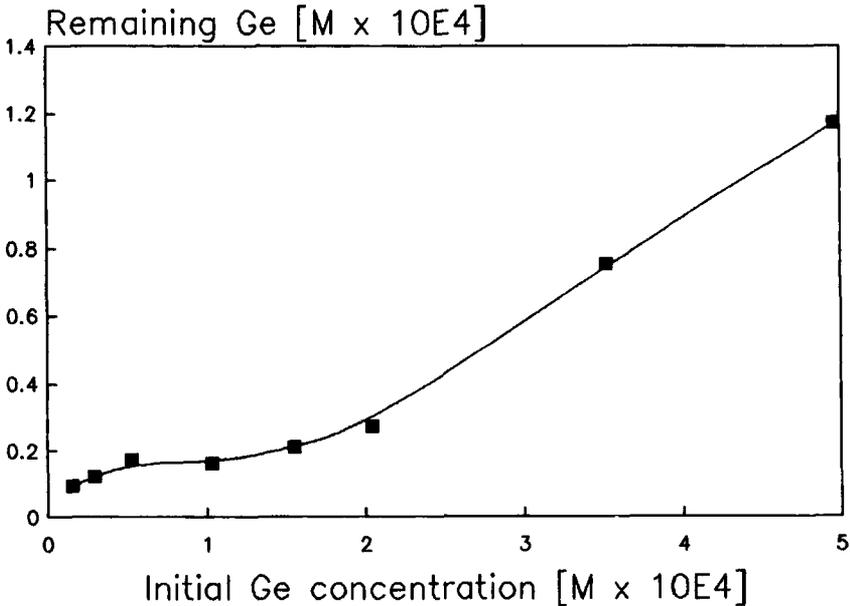


FIGURE 9

Ion flotation of germanium. Effect of initial Ge concentration on the amount remaining in solution ³³. Reprinted with permission; copyright 1988, Marcel Dekker, Inc.

a trial and error procedure. The factorial design of experiments offers the advantage of simultaneous change of all the variables, thereby obtaining quantitative estimation not only of the basic effects, but also of their interactions. This saves time and effort for the operator and real optimum conditions can be reached statistically. The disadvantage of this method, however, is that it needs a certain previous experience in the field.

The factorial design was used in the dissolved-air flotation of the CuS / ZnS ⁴⁶. The criteria of Student (t-test) and Fisher were used in the analysis of variance. Two series of batch experiments were conducted : an initial first-order series, considering as basic parameters the copper-ion concentration, pH and the

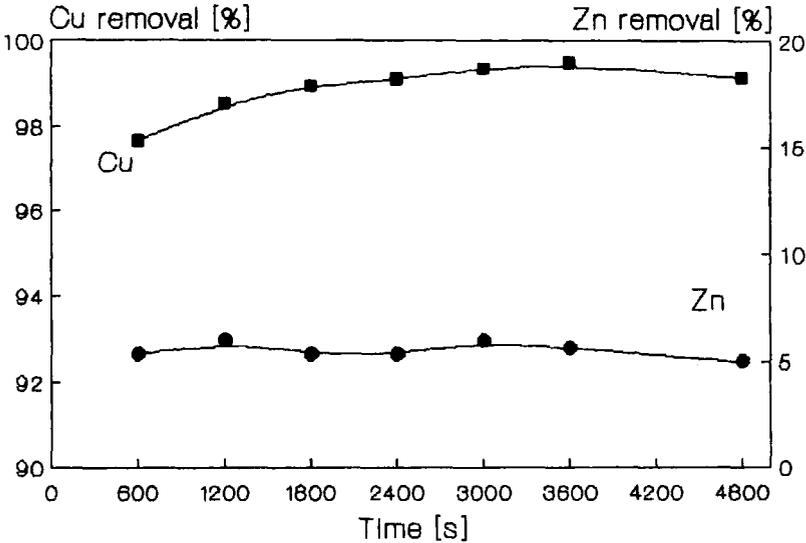


FIGURE 10

Separation of Cu/Zn as sulfides in continuous flow ⁴⁷. Reagents used : dodecylamine (collector) and cetyl-pyridinium chloride (frother). [Cu²⁺] = 50 ppm; [Zn²⁺] = 250 ppm. pH : 1.7 ± 0.1, gas flowrate 3.3 cm³.s⁻¹, Na₂S in 30% excess, mean residence time 1.2 ks. Reprinted with permission; copyright 1989, Marcel Dekker, Inc.

concentrations of sodium sulphide and amine added; and a second-order series, with the copper and zinc ion concentrations and the preliminary stirring speed as parameters. The separation results obtained from these experiments were considered as promising. Statistics and particularly the factorial design of experiments may be an extremely useful tool in flotation experimentation.

Process design theory developed for foam separation was based on its resemblance, in a way, with distillation with entrainment³. Mathematical modelling was further advanced by Wilson ⁵ and Schulze ¹, among others. Earlier, the batch flux analysis, known from the sedimentation of suspensions, was applied in dissolved-air-flotation treatment of wastewater ⁶⁷.

Batch flotation experiments are generally used to obtain data to evaluate a continuous flow flotation unit, to foresee the way it should work and predict the expected result. The basic information required from the batch tests are the following ⁶⁶ :

- 1) Will the metal being considered float?
- 2) How rapidly will it float (rate of flotation)?
- 3) What degree of removal can be expected?
- 4) What type of bubble generation method is suitable?
- 5) How do changes in operating conditions (feed concentration, air flowrate, pH, etc.) influence these answers?

The answers are important when one is considering the design of a flotation equipment for a particular separation. Attention should be paid, however, on the sensitivity of the process with respect to each application ²⁴.

An account of flotation machine development, in ore dressing was given by Barbery ⁶⁹ and Harris ¹³, together with the general principles governing the operation of the cells. The main effort has been to find the most suitable impeller design.

The efficiency of a flotation unit was expected to be a function of the residence time distribution of the species involved, so an investigation of the cell hydrodynamics was undertaken, assuming non-ideal flow ⁷⁰, i.e. by-passing or deadwater regions etc. Cells operating in backmixed or plug flow mode were investigated, using a stimulus-response technique in continuous cocurrent and counter-current flows and a theoretical model involving several parameters was developed. The modelling of liquid-phase mixing in a flotation column was also reported ¹⁵.

An examination of the operation from the kinetic point of view could also be helpful for design calculations, as presented by Ek ⁷¹. This may be carried out, in analogy with chemical reactions, trying the elementary reaction equations.

In the macroscopic method, which is the engineer's preferable method, a general product equation was first postulated ⁷², representing the kinetics of flotation :

$$\frac{dC}{dt} = -k_n i \cdot \Pi(C_i^{n_i})$$

where C_i represents the concentration of a particular constituent in the system (e.g., air, floatable or non-floatable material etc.), while n_i specifies the order.

The second method, which is strictly speaking more scientific, includes the direct application of physicochemical principles for the analysis of the different successive stages, that lead to the formation of the aggregate. Although this approach has yielded remarkable results, it is very difficult to apply it in industrial practice ⁷³.

The above equation, as it stands, was too complex; however, it was simplified by lumping all variables, except the concentration of floatable material and the concentration of air C_a , into the rate coefficient k_a , with some loss of generality :

$$\frac{dC}{dt} = -k_a \cdot C \cdot C_a^n$$

Now, k_a is a complex function involving, among others, reagents concentration, particle and bubble sizes, induction times, flotation cell design, rate of froth removal, previous treatment, power input etc.

Since the air supply is usually constant, any tendency for a change in air bubble concentration is usually small. Under these circumstances, the first-order kinetic equation :

$$(dC/dt) = kC$$

has been followed ⁷⁴. Usually, the assumption made for the order of the rate (dC/dt) is that it does not change during the whole flotation procedure, resulting in a constant value of the parameter k ; the latter, although not exactly true, is an acceptable simplification. A simple test of this assumption may be made by drawing on a semi-logarithmic plot the ratio of ion concentration

TABLE
Metals recovery from solutions by flotation

Metal	Technique	Reference
As	adsorbing colloid flotation of trivalent	34
	adsorbing colloid flotation (dissolved- and dispersed-air)	32
	adsorbing colloid flotation, in analysis	78
	adsorbing colloid flotation, in presence of heavy metals	45
	adsorbing colloid flotation, as hydride	61
	adsorbing colloid flotation, from seawater	60
	adsorbing colloid flotation of pontavalent	36
	ion flotation (electrolytic) by cationic collectors	25
Cr	ion flotation (dissolved-air), continuous by EHDA-bromide	26
	precipitate flotation, after reduction with ferrous sulfate	27
	ion flotation by rosin amine acetate	28
	ion flotation (dissolved- and dispersed-air) by dodecylamine	31,32
	precipitate flotation as hydroxide	41
	precipitate (foam) flotation, continuous	48
	precipitate flotation as sulfide (dissolved- air)	46
	precipitate flotation as sulfide, continuous	47
Cu	precipitate flotation as sulfides of heavy metals	42
	foam and bubble fractionation	43
	adsorbing colloid flotation, from seawater	44
	precipitate flotation as sulfide	45
	ion flotation by thio collectors	36
	ion flotation with monolauryl dithio- carbamate	38
	ion-precipitate ultrafine flotation	39
	ion flotation as soluble xanthate complex	40
	ion flotation, after activation with pyrogallol	32,33
	ion flotation, as various complexes	35
adsorbing colloid flotation by ferric sulfate-sodium oleate	34	
Ge	ion flotation, after activation with pyrogallol, scale-up aspects	50
	adsorbing colloid flotation, in analysis	78
	ion flotation-doctorate thesis	62
	precipitate flotation as hydroxide	6
	"foam" separation, as hydroxide	49
Pb	adsorbing colloid flotation, pilot plant	64
	precipitate flotation, in presence of germanium	50
	flotation-separation from zinc	76

TABLE (continued)
Metals recovery from solutions by flotation

Metal	Technique	Reference
Pb	ion flotation as chloride ions	53
	ion flotation in thiocyanate solutions	54
	foam flotation, trace metals	43
	precipitate flotation as sulfides of heavy metals	42
Zn	precipitate flotation as sulfide (dissolved-air)	46
	precipitate flotation as sulfides of heavy metals	42
	adsorbing colloid flotation from seawater	44
	ion exchange on zeolite and foam flotation	29
	ion flotation by thio collectors	36
	precipitate flotation as sulfide, continuous	47
	precipitate flotation as hydroxide, various collectors	51
	foam fractionation	52
	ion flotation as chloride anions	53
	ion flotation in thiocyanate solutions	54
	adsorbing colloid flotation (dissolved-air and dispersed-air)	55
	precipitate flotation (electrolytic)	56
	precipitate flotation-selective separation	77
	"precipitation-flotation", of heavy metals	45

over the initial one versus flotation time as a variable: if the assumption holds, this should yield a straight line. For example, in the case of germanium flotation, this equation was found to be in good agreement with the experimental results³³; the flotation rate constant, k , was calculated to be 0.008 s^{-1} .

Studies of the (electrolytic) flotation were earlier reported for the treatment of a paint effluent and an oil emulsion in pilot-plant tests^{23,24}, displaying first-order kinetics. The flotation coefficient was calculated as a function of time and from that the flotation rate was computed; this was found to reach a maximum at a certain concentration. A mass balance was used elsewhere for continuous-flow experiments⁷⁰.

The scale-up of the ion flotation process, while possible, needs attention, mainly in the retention time and flotation reagents addition. For example, in the case of germanium flotation with pyrogallol and dodecylamine ³³, the optimum experimental conditions determined in the small-scale apparatus (100 cm³), needed to be revised when the process was scaled-up and applied in a larger cell (with a volume of 2000 cm³) ⁵⁰. A nearly 100% stoichiometric excess of reagents was required to achieve the same results as in the small cell; retention time had also to be increased by four times.

In scaling-up experiments ²⁴, it was realized that the rate of flotation decreased, which meant longer retention times. Two reasons were given: the wall effects in the small vessel and the internal reflux of suspended matter from the disturbed froth.

Generally, the principles of reactor design and scale-up are well established in chemical technology ⁷⁵. This knowledge would not only benefit operation of cells and prediction of performance, but the design of flotation plants would be based on a surer foundation, too. The excessive reliance on costly trial-and-error development of new and improved units could also be reduced.

6. SELECTIVE SEPARATION BY FLOTATION

Selective separation of metals in aqueous solutions presents, according to our belief, a valid reason for the future application of the process to hydrometallurgy. There are not many papers in the bibliography on this area, compared with this significant advantage of flotation. In the following, some of them will be reviewed.

One of the systems investigated was the precipitate flotation of calcium sulfide from calcium sulfate in dilute aqueous solutions, using an anionic collector ⁷⁶. Selective separation by flotation was also the field covered by Charewicz ⁷¹; the Polish

group at Wroclaw University has done exceptional work, for example in the field of chloride complexation of metals.

The selectivity of the process was also examined while separating lead from zinc ions ⁶². While precipitating the ions as sulfides - previously precipitated as hydroxides - a difference in behavior was observed concerning mainly the collector (dodecylamine) consumption. This was probably due to the difference in solubilities of the respective substances. Hence, it was proposed that a selective separation of zinc from lead could be achieved by adjusting the amount of collector used.

In another study of the precipitate flotation of zinc, cobalt and copper as hydroxides using sodium dodecylsulfate as an anionic collector ⁷⁷, it was proved that selective separation was possible.

Figure 3 has already illustrated the possibility of germanium and arsenic co-flotation ³⁴. Trace levels of germanium, antimony, arsenic and selenium from a boric acid solution were also simultaneously concentrated using adsorbing colloid flotation as an analytical technique ⁷⁸.

Lead was also successfully separated from germanium - both precipitated as hydroxides at pH 10 - using dodecylamine as a collector ⁵⁰. A crucial parameter of the process was found to be the ratio of dodecylamine concentration over lead ion concentration, often symbolised as " ϕ " (collector to colligend ratio). A reverse flotation was observed, giving lead in the foam layer while germanium was left in solution; lead recoveries were usually over 80%. Figure 4 illustrates some of the results, discussed above.

Copper/zinc ions were separated in continuous flow precipitate flotation as sulfides ⁴⁷, with dodecylamine (5 ppm in 0.025% ethanolic solution) (Fig. 10). Copper was first precipitated in a highly acidic medium, with pH 1.7; recoveries of copper reached 95%. Zinc was then precipitated, at pH 5.0, in a second separation stage. Selectivity could be achieved by carefully selecting the operating conditions. The ratio " ϕ " was in the range from 0.1

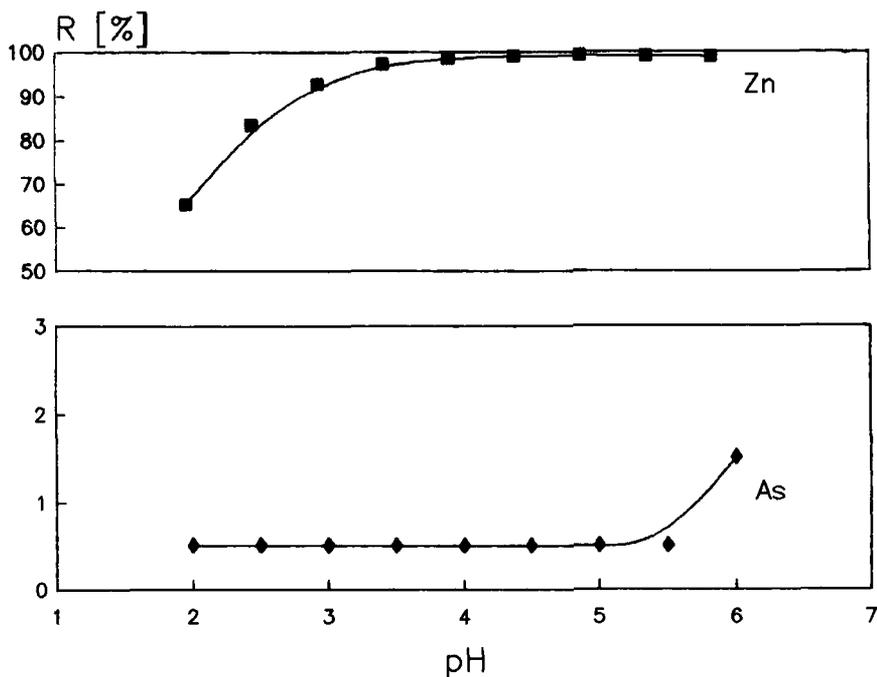


FIGURE 11

Selective flotation of Zn ions from Zn/As with a stoichiometric amount of diethyldithiocarbamate (50 ppm) ³⁶. Reprinted with permission; copyright 1989, Marcel Dekker, Inc.

up to 0.2, being higher in the more dilute cases (initial ion concentration 50 ppm). A small amount (5 ppm) of cetyl-pyridinium chloride was also necessary to stabilize the foam. It was also found that the preliminary mixing, in the precipitation - coagulation stage was critical, mixing time and impeller speed being most important.

The selective separation of copper, zinc and (pentavalent) arsenic from solution by dissolved-air flotation techniques was investigated, too ³⁶. A dialkyl-dithiocarbamate (DTC) was applied first for the zinc ion flotation (Fig. 11). DTC acts as an anionic collector, precipitating zinc. Zinc recoveries over 95%, in the

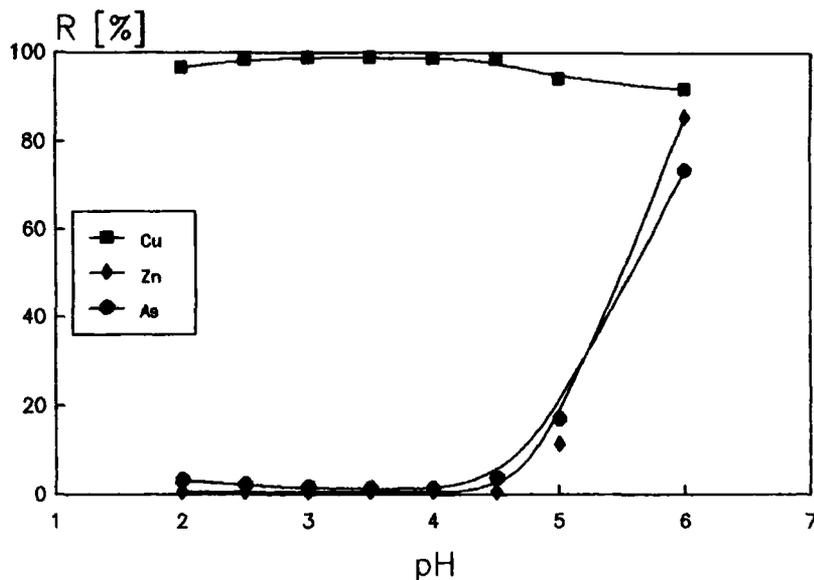


FIGURE 12

Selective flotation of Cu ions from Cu/Zn/As(V) with KEX³⁶. Initial concentration of all ions 50 ppm, 10% excess of KEX. Reprinted with permission; copyright 1989, Marcel Dekker, Inc.

pH range of 3.5 to 6.0, were found. Arsenic ions were next removed by adsorbing colloid flotation on hydrolysed ferric sulfate.

Copper / zinc / arsenic ions were also floated by a short-chain xanthate as collector³⁶ (Fig. 12). Promising results were observed in the pH range of approximately 2.0 - 4.7 for the selective separation of copper ions. At higher pH values, a pronounced co-flotation of all the heavy metals was noticed. An increased presence of the $H_2AsO_4^-$ species was noted, caused by the increase in the solution pH.

It was also observed that zinc remained in solution almost quantitatively. This could be explained by the solubility products of the metal ions with ethyl xanthate, which are 4.9×10^{-9} for zinc, but only 5.2×10^{-20} for copper³⁷. This indicates that

copper could be selectively precipitated and then floated by fine air bubbles.

Concluding, it is believed that the aspect of selective separation by flotation constitutes the most important potential of the process, contributing in this way in the recycling of metals. The various applications given in the present review (not including the books) are summarised in the following table, with comments in each case.

It is true that, so far, only mineral process and sanitary (or public health) engineers have dealt with the process of flotation. Some gaps still exist, especially from the chemical engineering point of view, preventing its wider large-scale application in chemical industry. Bringing together scientists from all the fields involved⁷⁹ will probably help and give a thrust for future development.

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NOMENCLATURE

aF : flotation activity
 C : species concentration
 Ca : air concentration
 Ci : concentration of i-th species
 Co : initial concentration
 k : kinetic rate constant
 Ka : kinetic rate constant
 Kb : kinetic rate constant
 kni : kinetic rate constant
 Kso : kinetic rate constant
 Ks1 : kinetic rate constant
 R : flotation removal or recovery
 t : time

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